



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 460 057 A1**

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:
22.09.2004 Bulletin 2004/39

(51) Int Cl.7: **C07C 69/653, C07C 35/52**

(21) Application number: **02786177.2**

(86) International application number:
PCT/JP2002/013378

(22) Date of filing: **20.12.2002**

(87) International publication number:
WO 2003/055841 (10.07.2003 Gazette 2003/28)

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SI SK TR**

(30) Priority: **25.12.2001 JP 2001390972**
30.07.2002 JP 2002220729
07.11.2002 JP 2002324257

(71) Applicant: **IDEMITSU PETROCHEMICAL CO.,
LTD.**
Tokyo 130-0015 (JP)

(72) Inventors:
• **TANAKA, Shinji**
Chiba (JP)

• **YOSHITOME, Toshihide**
Chiba (JP)
• **KODOI, Kouchi**
Chiba (JP)
• **ONO, Hidetoshi**
Chiba (JP)
• **HATAKEYAMA, Naoyoshi**
Chiba (JP)

(74) Representative: **Prop, Gerrit**
Brucknerstrasse 20
40593 Düsseldorf (DE)

(54) **PERFLUOROADAMANTYL ACRYLATE COMPOUND AND INTERMEDIATE THEREFOR**

(57) A perfluoroadamantyl acrylate compound which is highly useful as a raw material for functional resins, etc.; and an intermediate therefore. The perfluoroadamantyl acrylate compound comprises perfluoroadamantane having a $\text{CH}_2 = \text{C(R)COO}$ group(wherein R

is a hydrogen atom, a methyl group or a trifluoromethyl group) at the 1-position, at each of the 1- and 3-positions, at each of the 1-,3- and 5-positions, at each of the 1-,3-,5- and 7-positions, or at the 2-position.

EP 1 460 057 A1

Description

TECHNICAL FIELD

5 [0001] The present invention relates to a novel perfluoroadamantyl compound and an intermediate therefor, and more particularly, to a novel perfluoroadamantyl compound and an intermediate therefor that are highly useful as a raw material for functional resins.

BACKGROUND ART

10 [0002] It is known that an acrylic ester and a methacrylic ester each having an adamantane skeleton can be polymerized into a polymer which is excellent in heat resistance, mechanical strength such as impact resistance and surface hardness and optical characteristics. For instance, Japanese Patent Laid-Open Application (No. 307844/1988 (Showa 63)) proposes a diacrylate and dimethacrylate having a halogen atom or a hydroxy group at each of the 5-position of the adamantane skeleton or at each of the 7-position of the same. The acrylic ester and methacrylic ester each having the above-mentioned structural unit, which are colorless and transparent and have high a surface hardness and also large refractive index, are highly useful as a raw material for optical instruments and members such as lens, prisms, photosensitive materials, optical fiber and optical discs. In addition, the acrylic ester and methacrylic ester as mentioned above have each a surpassingly high melting point and surface hardness as compared with the acrylic ester and methacrylic ester that are being generally used, are highly useful as a material of a heat resistant covering and forming for an acrylic ester and methacrylic ester. However the aforesaid useful acrylic ester and methacrylic ester suffer from a disadvantage of insufficient transparency in a low wavelength region.

15 [0003] As mentioned hereinbefore, the acrylic ester and a methacrylic ester each having an adamantane skeleton which is imparted with a specific chemical structure are highly useful as a raw material for a functional resin. However it is desired to develop an acrylic ester and a methacrylic ester which have any of various chemical structures and which are capable of being made into an acrylic ester and a methacrylic ester, respectively that are enhanced in such functionality as optical properties and heat resistance.

DISCLOSURE OF THE INVENTION

20 [0004] An object of the present invention is to provide a perfluoroadamantyl acrylate compound which is highly useful as a material for functional resins and the like; and an intermediate therefor.

25 [0005] As the result of intensive extensive research and investigation accumulated by the present inventors in order to achieve the object as mentioned above, it has been found that a perfluoroadamantyl acrylate compound having a specific chemical structure can achieve the above-mentioned object. Thus the present invention has been accomplished on the basis of the foregoing findings and information.

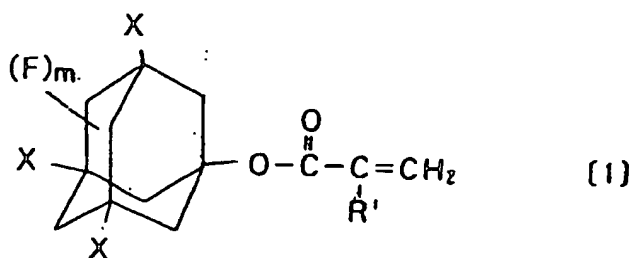
30 [0006] Specifically, the gist of the present invention is as follows.

(1) A perfluoroadamantyl acrylate compound represented by the following general formula (1)

40

45

50



55 wherein R' is a hydrogen atom, a methyl group or a trifluoromethyl group; X is a fluorine atom, a hydroxy group or a $\text{CH}_2 = \text{C}(\text{R})\text{COO}$ group, wherein R is a hydrogen atom, a methyl group or a trifluoromethyl group; and m is an integer of from 12 to 15.

(2) A perfluoroadamantyl acrylate compound represented by the following general formula (2)



15

20



30

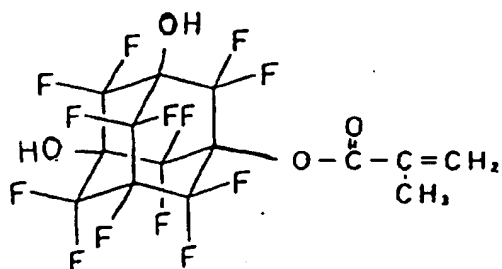
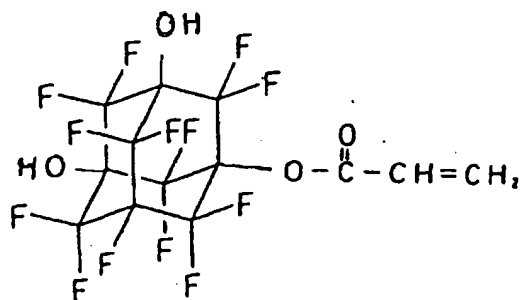
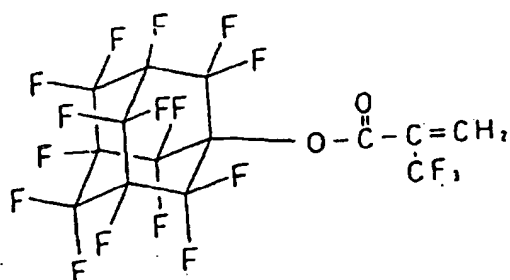
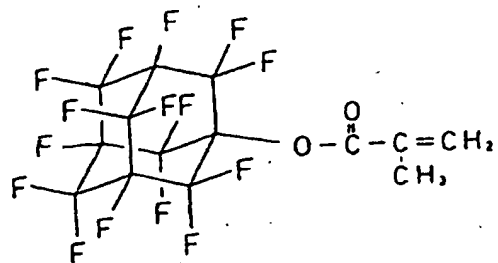
35

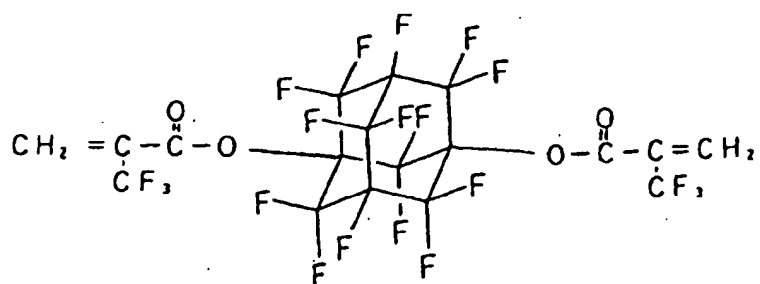
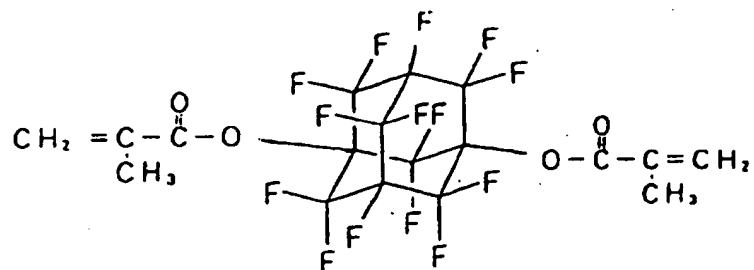
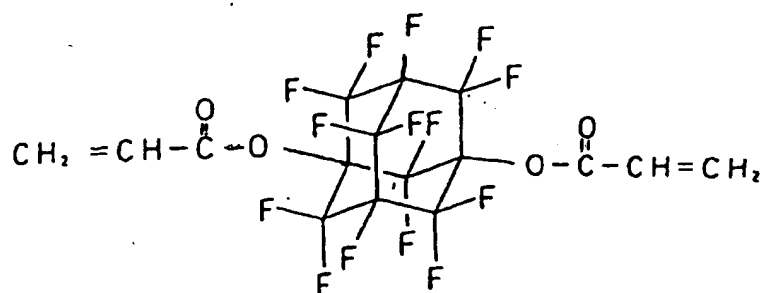
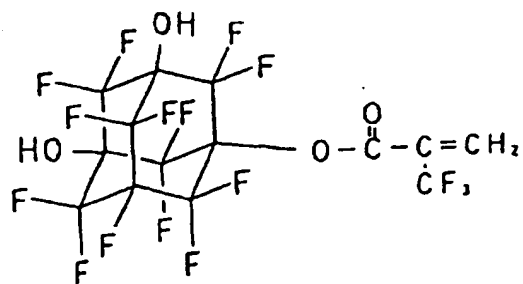
40

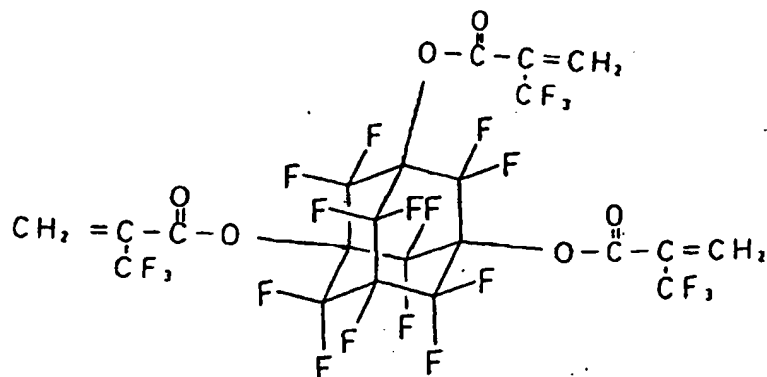
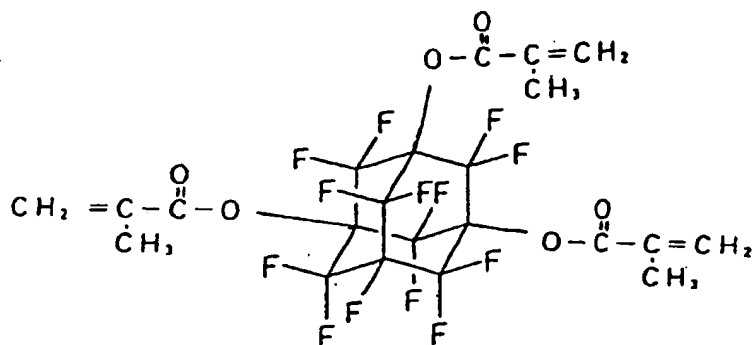
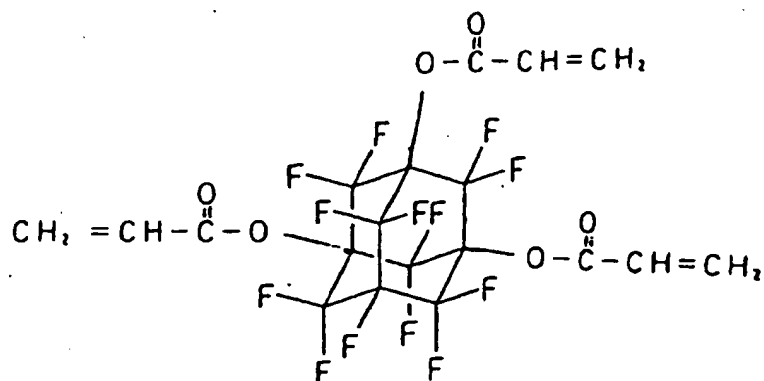
45



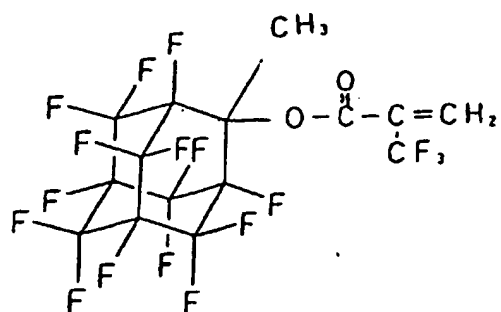
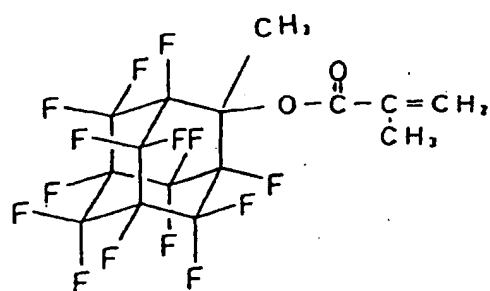
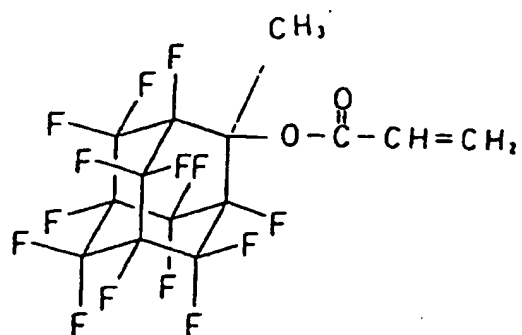
55

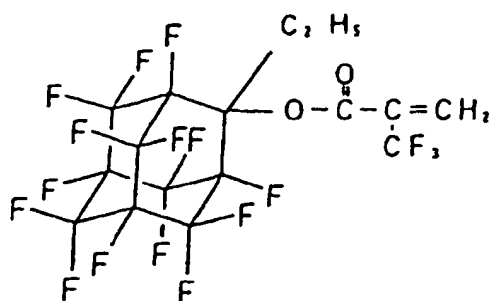
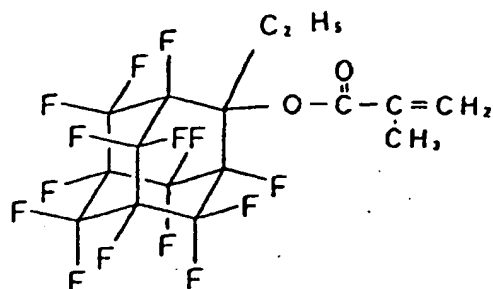
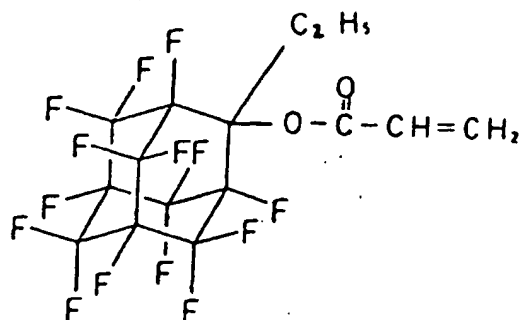






50 The perfluoroadamantyl acrylate compounds represented by the general formula (2) according to the present invention are specifically exemplified by





50 The perfluoroadamantyl acrylate compounds represented by the general formula (3) according to the present invention are specifically exemplified by 2-methyl-2-perfluoroadamantanol, 2-ethyl-2-perfluoroadamantanol, 2-trifluoromethyl-2-perfluoroadamantanol, 2-pentafluoroethyl-2-perfluoroadamantanol, 2-heptafluoropropyl-2-perfluoroadamantanol, and 2-nonafluorobutyl-2-perfluoroadamantanol. Next, a process for producing a perfluoroadamantyl acrylate compound represented by the general formula (1) can be in accordance with a process which comprises azeotropically dehydrating a perfluoroadamantanol and an acrylic acid or an analog thereof under reflux of a solvent. Examples of the perfluoroadamantanol to be used as a starting raw material include perfluoro-1-adamantanol, perfluoro-1,3-adamantandiol, perfluoro-1,3,5-adamantanetriol and perfluoro-1,3,5,7-adamantanetetraol. Examples of the acrylic acid or an analog thereof include acrylic acid, methacrylic acid and α -trifluoromethyl acrylate. As a reaction solvent, toluene and xylene are preferably used.

[0009] In addition, the reaction conditions in this case, which are similar to those in a general azeotropic dehydration reaction, can be set on a reaction temperature in the range of minus 78 to 200°C, but is preferably set on the boiling point of the solvent at the reaction pressure at this time, including a reaction pressure in the range of 0.1 to 10 MPa, a reaction time in the range of 1 to 24 hours, preferably 3 to 6 hours. The concentration of the starting raw material to be dissolved in the reaction solvent needs only to be within the saturated solubility without specific limitation, but is preferably in the range of 0.5 to 1.0 mol / liter.

[0010] In a process for producing the perfluoroadamantyl acrylate compound represented by the general formula (2) according to the present invention, the starting raw material needs only to use a perfluoroadamantanol such as 2-H-2-perfluoroadamantanol, 2-methyl-2-perfluoroadamantanol, 2-ethyl-2-perfluoroadamantanol, 2-trifluoromethyl-2-perfluoroadamantanol and 2-pentafluoroethyl-2-perfluoroadamantanol, and the reaction conditions in this case need only to be similar to the foregoing.

[0011] Further, the reaction of the perfluoroadamantanol and the acrylic acid or analogues in the production of these perfluoroadamantyl acrylate compounds may be put into practice by dehydration esterification by the use of a dehydrating agent. In the case of this production process, the dehydrating agent is preferably selected for use from molecular sieves that are used for general dehydration esterification and acidic dehydrating agents such as sodium sulfate anhydride, magnesium sulfate anhydride and phosphoric acid anhydride. As a reaction solvent, use is made of an ether base solvent such as diethyl ether, tetrahydrofuran and dioxane; and an aliphatic hydrocarbon base solvent such as hexane, heptane and octane; and aromatic hydrocarbon base solvent such as benzene, toluene and xylene. In addition, the reaction conditions in this case can be set on a reaction temperature in the range of minus 78 to 200°C, but is preferably set in the range of room temperature to the boiling point of the solvent at the reaction pressure at this time, including a reaction pressure in the range of 0.1 to 10 MPa, preferably atmospheric pressure, a reaction time in the range of 1 to 24 hours, preferably 3 to 6 hours. The concentration of the starting raw material to be dissolved in the reaction solvent needs only to be within the saturated solubility without specific limitation, but is preferably in the range of 0.5 to 1.0 mol / liter.

[0012] The perfluoroadamantyl acrylate compounds can be produced by esterification reaction in the presence of a base between a perfluoroadamantanol and an acrylic acid chloride or an analog thereof. Examples of the base to be used therein include trimethylamine, triethylamine, pyridine and N,N-dimethylaniline. As a reaction solvent, which is not always necessary, use can be made of halogenated hydrocarbons such as dichloromethane, carbon tetrachloride and 1,2-dichloroethane; an ether base solvent such as diethyl ether, tetrahydrofuran and dioxane; and an aliphatic hydrocarbon base solvent such as hexane, heptane and octane; and aromatic hydrocarbon base solvent such as benzene, toluene and xylene. In addition, the reaction conditions in this case can be set on a reaction temperature in the range of minus 78 to 100°C, but is preferably set in the range of minus 78 to room temperature, including a reaction pressure in the range of 0.1 to 10 MPa, a reaction time in the range of 1 to 24 hours, preferably 1 to 3 hours. In the case where a reaction solvent is used, the concentration of the starting raw material to be dissolved in the reaction solvent needs only to be within the saturated solubility without specific limitation, but is preferably in the range of 0.5 to 1.0 mol / liter.

[0013] The perfluoroadamantyl acrylate compounds can be produced by esterification reaction between a perfluoroadamantyl alkoxide and an acrylic acid chloride or an analog thereof. As a reaction solvent, use can be made of an aliphatic hydrocarbon base solvent such as hexane, heptane and octane; and aromatic hydrocarbon base solvent such as benzene, toluene and xylene. In addition, the reaction conditions in this case can be set on a reaction temperature in the range of minus 78 to 100°C, but is preferably set in the range of minus 78 to room temperature, including a reaction pressure in the range of 0.1 to 10 MPa, a reaction time in the range of 1 to 24 hours, preferably 1 to 3 hours. In the case where a reaction solvent is used, the concentration of the starting raw material to be dissolved in the reaction solvent needs only to be within the saturated solubility without specific limitation, but is preferably in the range of 0.5 to 1.0 mol/liter.

[0014] The perfluoroadamantyl alkoxide to be used in the reaction can be produced by reacting the above-mentioned perfluoroadamantanol with an alkoxidizing agent. As the alkoxidizing agent, use is made of metallic lithium, metallic sodium, metallic potassium, n-butyllithium, sec-butyllithium, tert-butyllithium, sodium hydroxide, sodium hydride, sodium boron hydride and lithium-aluminum hydride. As a reaction solvent, use is made of an ether base solvent such as diethyl ether, tetrahydrofuran and dioxane; an aliphatic hydrocarbon base solvent such as hexane, heptane and octane; and aromatic hydrocarbon base solvent such as benzene, toluene and xylene.

[0015] The acrylic acid chloride or an analog thereof to be used in the reaction can be produced by reacting a chlorinating agent with the above-mentioned acrylic acid chloride or an analog thereof. As the chlorinating agent, there are preferably used thionyl chloride, phosphorus pentachloride, phosphorus trichloride, benzoic acid chloride and phthalic acid chloride. In this reaction, as a reaction solvent, which is not always necessary, use can be made of halogenated hydrocarbons such as dichloromethane, chloroform, carbon tetrachloride and 1,2-dichloroethane; an aliphatic hydrocarbon base solvent such as hexane, heptane and octane; and aromatic hydrocarbon base solvent such as benzene, toluene and xylene. There may be used as necessary, a catalyst such as N,N-dimethylformamide, hexamethylphos-

phoric triamide and pyridine; and a reaction accelerator such as benzytriethylammonium chloride.

[0016] In addition, the reaction conditions in this case can be set on a reaction temperature in the range of 0 to 200°C, preferably room temperature to 100°C, including a reaction pressure in the range of 0.1 to 10 MPa, a reaction time in the range of 1 to 24 hours, preferably 1 to 6 hours. In the case where a reaction solvent is used, the concentration of the starting raw material to be dissolved in the reaction solvent needs only to be within the saturated solubility without specific limitation, but is preferably in the range of 0.5 to 1.0 mol / liter.

[0017] In the last place, description will be given of some processes for producing the perfluoroadamantanol represented by the general formula (3), wherein perfluoro-2-adamantanone is used in every case as a starting raw material.

(1) In the case of R³ being a methyl group or an ethyl group

(a) addition reaction to carbonyl group with a Grignard reagent The starting raw material and the Grignard reagent are reacted in a solvent and the reaction product is hydrolyzed with an acid. As a reaction solvent, use is made of an ether base solvent such as diethyl ether, tetrahydrofuran and dioxane; an aliphatic hydrocarbon base solvent such as hexane, heptane and octane; and aromatic hydrocarbon base solvent such as benzene, toluene and xylene. As a Grignard reagent, use is made of an alkyl magnesium chloride (RMgCl), alkyl magnesium bromide (RMgBr) and alkyl magnesium iodide (RMgI). The reaction conditions in the first half stage include atmospheric pressure, reaction temperature in the range of minus 78 to 200°C, preferably 0°C to room temperature, a reaction time in the range of 1 to 24 hours. In the case where a reaction solvent is used, the concentration of the starting raw material to be dissolved in the reaction solvent needs only to be within the saturated solubility without specific limitation, but is preferably in the range of 0.5 to 1.0 mol / liter.

(b) addition reaction to carbonyl group with a lithium reagent The starting raw material and the lithium reagent are reacted in a solvent and the reaction product is hydrolyzed with an acid. As a reaction solvent, use is made of an ether base solvent such as diethyl ether, tetrahydrofuran and dioxane; an aliphatic hydrocarbon base solvent such as hexane, heptane and octane; and aromatic hydrocarbon base solvent such as benzene, toluene and xylene. As a lithium reagent, use is made of an alkyl lithium (RLi) and dialkylmethylmagnesium cuprate (R₂ LiCu). The reaction conditions in the first half stage include atmospheric pressure, reaction temperature in the range of minus 78 to 200°C, preferably 0°C to room temperature, a reaction time in the range of 1 to 24 hours. In the case where a reaction solvent is used, the concentration of the starting raw material to be dissolved in the reaction solvent needs only to be within the saturated solubility without specific limitation, but is preferably in the range of 0.5 to 1.0 mol / liter.

(2) In the case of R³ being R_f (perfluoroalkyl group: CF₃~C₄F₉)

(a) addition reaction to carbonyl group with a trimethylsilanyl perfluoroalkane [RfSi(CH₃)₃]

The starting raw material and the trimethylsilanyl perfluoroalkane [RfSi(CH₃)₃] are reacted in a solvent in the presence of a catalyst, and the reaction product is hydrolyzed with an acid. As a reaction solvent, use is made of an ether base solvent such as diethyl ether, tetrahydrofuran and dioxane; an aliphatic hydrocarbon base solvent such as hexane, heptane and octane; and aromatic hydrocarbon base solvent such as benzene, toluene and xylene. As a catalyst, use is made of tetrabutylammonium fluoride [(C₄H₉)₄NF]. The reaction conditions in the first half stage include atmospheric pressure, reaction temperature in the range of usually minus 78 to 200°C, preferably 0°C to room temperature, a reaction time in the range of usually 1 to 24 hours. In the case where a reaction solvent is used, the concentration of the starting raw material to be dissolved in the reaction solvent needs only to be within the saturated solubility without specific limitation, but is preferably in the range of 0.5 to 1.0 mol / liter.

(b) addition reaction to carbonyl group with a perfluoroalkyl iodide (Rfi)

The starting raw material and the perfluoroalkyl iodide (Rfi) are reacted in a solvent in the presence of a catalyst, and the reaction product is hydrolyzed with an acid. As a reaction solvent, use is made of an ether base solvent such as diethyl ether, tetrahydrofuran and dioxane; an aliphatic hydrocarbon base solvent such as hexane, heptane and octane; N,N-dimethylformamide and dimethylsulfoxide. As a catalyst, use is made of Zinc (Zn)/ dicyclopentadienyltitanium dichloride (Cp₂ TiCl₂) (coexisting system). The reaction conditions in the first half stage include atmospheric pressure, reaction temperature in the range of usually minus 78 to 200°C, preferably 0°C to 100°C, a reaction time in the range of usually 1 to 24 hours. In the case where a reaction solvent is used, the concentration of the starting raw material to be dissolved in the reaction solvent needs only to be within the saturated solubility without specific limitation, but is preferably in the range of 0.5 to 1.0 mol / liter. It is preferable in this reaction to simultaneously apply ultrasonic activation by means of a ultrasonic cleaner.

The perfluoroadamantyl acrylate compound obtainable in the above-mentioned manner according to the

present invention is excellent in such characteristics as heat stability, chemical stability, lubricity and electrical insulation properties and thus is highly useful in wide fields of raw materials for functional resins required of optical properties and heat resistance; resin additives such as heat resistance improvers; additives such as acidity enhancers and fat-solubility enhancers; coating materials such as paint and printing ink; lubricating oil; working oil; heating / heat transfer media; adhesives; covering materials for optical fiber; pharmaceuticals; agrochemicals; intermediates and so forth.

EXAMPLE

- [0018]** In what follows, the present invention will be described in more detail with reference to comparative examples and working examples, which however shall never limit the present invention thereto.

Example 1

- [0019]** In a 50 milliliter (mL) flask was placed 2.1 g (5.0 millimol) of perfluoroadamantanediol and then were added 10 mL of tetrahydrofuran as a solvent and 0.84 mL (6.0 millimol) of triethylamine as a base with stirring. Subsequently the flask was put in an ice bath, and 0.4 mL (5.0 millimol) of acrylic acid chloride was gradually added dropwise in the flask. When the acrylic acid chloride was added dropwise, a salt was immediately formed, causing the reaction liquid to become whitely turbid. After the lapse of 15 minutes from the end of the dropwise addition, the flask was taken out from the ice bath, and the mixture therein was reacted for 3 hours at room temperature with stirring.

- [0020]** After the completion of the reaction, the resultant reaction liquid was filtered with a cannula equipped with a filter, and the inside of the flask was washed twice with 5 mL of tetrahydrofuran. Subsequently the solvent was evaporated away from the reaction liquid. Thus the reaction liquid was purified with a glass tube oven to obtain the objective perfluoro-1-adamantyl acrylate with a yield amount of 1.4 g (2.9 millimol) and a yield rate 59.0%.

- [0021]** As a result of analysis for the resultant perfluoro-1-adamantyl acrylate by nuclear magnetic resonance spectra (NMR), there were observed the following absorption. ¹H-NMR {270 MHz} : at 6.16 (dd, J_{vic-trans} = 10.4 Hz, J_{gem} = 1.5 Hz, 1H),

6.25 (dd, J_{vic-trans} = 10.4 Hz, J_{vis-clis} = 16.3 Hz, 1H), 6.64 (dd, J_{vic-clis} = 16.3 Hz, J_{gem} = 1.5 Hz, 1H).

¹³C-NMR {68 MHz} : at 123.4, 136.12, 157.47.

- [0022]** ¹⁹F-NMR {254 MHz} : at -221.55 (s, 3F), -121.17 (s, 6F), -114.62 (s, 6F).

In addition, the results of gas-chromatography mass spectrometric analysis were 476 (M⁺, 2.4%), 456 (1.8%), 55(100%).

Example 2

- [0023]** The procedure in Example 1 was repeated to obtain the objective perfluoro-1-adamantyl acrylate except that 0.49 mL (5.0 millimol) of methacrylic acid chloride was used in place of the acrylic acid chloride as the starting raw material. The yield amount was 1.6 g (3.3 millimol) and yield rate 65.0%.

- [0024]** As a result of analysis for the resultant perfluoro-1-adamantyl acrylate by nuclear magnetic resonance spectra (NMR), there were observed the following absorption.

[0025] ¹H-NMR {270 MHz} : at 3.03 (s, 3H), 5.88 (s 1H), 6.33 (s, 1H).

[0026] ¹³C-NMR {68 MHz} : at 18.34, 130.46, 158.79.

[0027] ¹⁹F-NMR {254 MHz} : at -221.65 (s, 3F), -121.18 (s, 6F), -114.55 (s, 6F).

- [0028]** In addition, the results of gas-chromatography mass spectrometric analysis were 490 (M⁺, 20%), 471 (19%), 69(100%).

Example 3

(1) Production of α -(trifluoromethyl)acrylic acid chloride

- [0029]** In a 200 mL flask was placed 42.0 g (300 millimol) of α -(trifluoromethyl) acrylic acid, to which was gradually added 70.0 mL (450 millimol) of phthalic dichloride at room temperature with stirring. Subsequently, by reacting the contents in the flask for 2 hours, while heating in an oil bath at 135°C, an orange reaction liquid was obtained.

- [0030]** Subsequently, by atmospherically distilling the reaction liquid, 41.2 g (yield rate 86.6%) of colorless transparent product in liquid form was obtained.

[0031] As a result of analysis for the resultant perfluoro-1-adamantyl acrylate by nuclear magnetic resonance spectra (NMR), there were observed the following absorption.

[0032] ¹H-NMR {270 MHz} : at 6.91 (s, 1H), 7.11 (s, 1H).

[0033] ^{13}C -NMR {68 MHz} : at 120.91 (quar, $J_{\text{C-F}} = 273.9$ Hz),

[0034] 135.25 (quar, $J_{\text{C-CF}_3} = 31.8$ Hz), 139.28, 161.92.

[0035] Thereby, the colorless transparent product was identified as α -(trifluoromethyl)acrylic acid chloride.

5 (2) Production of perfluoro-1-adamantyl- α -(trifluoromethyl) acrylate

[0036] The procedure in Example 1 was repeated to obtain the objective perfluoro-1-adamantyl- α -(trifluoromethyl) acrylate except that 801 mg (5.1 millimol) of the α -(trifluoromethyl) acrylic acid chloride which had been obtained in the preceding item (1).

10 [0037] The yield amount was 1.2 g (2.2 millimol) and yield rate was 44%.

[0038] As a result of analysis for the resultant perfluoro-1-adamantyl- α -(trifluoromethyl) acrylate by nuclear magnetic resonance spectra (NMR), there were observed the following absorption.

[0039] ^1H -NMR {270 MHz} : at 7.92 (quar, $J = 2.8$ Hz, 1H), 8.04 (quar, $J = 2.8$ Hz, 1H)

[0040] ^{13}C -NMR {68 MHz} : at 121.15 (quar, $J_{\text{C-F}} = 268.5$ Hz),

15 131.85 (quar, $J_{\text{C-CF}_3} = 5.0$ Hz), 132.74 (quar, $J_{\text{C-CF}_3} = 31.8$ Hz), 159.79.

[0041] ^{19}F -NMR {254 MHz} : at -221.51 (s, 3F), -121.99 (s, 6F), -114.44 (s, 6F), -66.41 (s, 3F)

[0042] In addition, the results of gas-chromatography mass spectrometric analysis were 544 (M^+ , 5.4%), 523 (4.3%), 123 (100%).

20 Example 4

(1) Production of 2-methyl-2-perfluoroadamantanol

[0043] In a 500 mL Kjeldahl flask was placed 24.1 g (60 millimol) of 2-perfluoroadamantanone, to which was added
25 180 mL of dry diethyl ether to dissolve the same. Thereafter the flask was put in an ice bath and 21 mL (63 millimol) of 3 mol/liter solution of methylmagnesium bromide was added dropwise in the flask with stirring. After the lapse of 30 minutes, gas-chromatographic analysis was carried out with a result that the disappearance of the raw material peak was confirmed. After the reaction liquid was poured on ice water, dilute hydrochloric acid was added so as to dissolve inorganic substances in a water phase. Organic phase was separated with a separatory funnel and dried. Then by
30 evaporating away the solvent, 22.9 g of a crude product was obtained, purified with a column, and recrystallized from methanol-hexane to obtain the objective product.

[0044] The yield amount was 8.1 g (19.4 millimol) and yield rate was 32.3%. Purity measured by gas chromatography was 84.1% [area].

[0045] As a result of analysis for the resultant 2-methyl-2-perfluoroadamantanol by nuclear magnetic resonance spectra (NMR), there were observed the following absorption.

[0046] ^1H -NMR {500 MHz} : at 1.81 (s, 3H, CH_3),

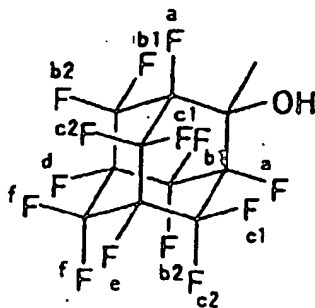
[0047] ^{13}C -NMR {126 MHz} : at 19.68 (t, $J = 13.2$ Hz, CH_3)

[0048] ^{19}F -NMR {471 MHz} : at -223.11 (s, 1F, d or e), -222.21 (s, 1F, d or e), -217.94 (s, 2F, a), -123.62 (quar, $J = 240$ Hz, 1F), -121.11 (s, 2F, f), -118.52 (d, $J = 240$ Hz, 1F), -117.46 (s, 1F), -116.90 (s, 1F), -116.34 (s, 1F), -114.39 (d, $J = 271$ Hz, 2F)

40 [0049] In addition, the results of gas-chromatography mass spectrometric analysis were 418 (M^+ , 0.38%), 403 (6.0%), 131 (85.2%), 69 (100%).

[0050] The melting point measured by DSC (differential scanning calorimetry) was 69.7 to 79.5°C.

[0051] As the result of structural analysis by the above-mentioned spectroscopic data, the following structural formula has been confirmed.



(2) Production of 2-methyl-2-perfluoroadamantyl methacrylate

[0052] In a 50 mL Kjeldahl flask was placed 0.836 g (2.0 millimol) of 2-methyl-2-perfluoroadamantanol, to which was added 20 mL of tetrahydrofuran to dissolve the same. Thereafter the flask was put in an ice bath, and 0.33 mL (2.4 millimol) of triethylamine and 0.22 mL (2.0 millimol) of methacrylic acid chloride were added in the flask to start stirring. After the lapse of 15 minutes, the ice bath was taken out, and the contents therein were reacted for further 48 hours at room temperature. The reaction liquid was filtered with fluted filter paper, and the flask was washed twice with 5 mL of diethyl ether. Salts were removed from the reaction liquid with a separatory funnel to recover organic phase. Then by distilling away the solvent and purifying with a column, the objective 2-methyl-2-perfluoroadamantyl methacrylate was obtained,

[0053] The yield amount was 0.17 g (0.35 millimol) and yield rate was 17.5%. Purity measured by gas chromatography was 97.6% [area].

[0054] As a result of analysis for the resultant 2-methyl-2-perfluoroadamantyl methacrylate by nuclear magnetic resonance spectra (NMR, CDCl_3), there were observed the following absorption.

[0055] $^1\text{H-NMR}$ (500 MHz) : at 1.93 (s, 3H, f), 2.16 (s, 3H, c), 5.71 (s, 1H, a1), 6.12 (s, 1H, a2)

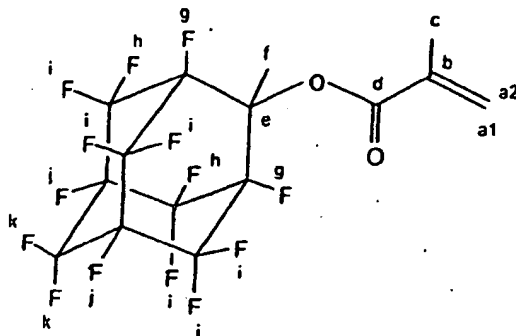
[0056] $^{13}\text{C-NMR}$ (126 MHz) : at 15.04 (f), 18.31 (c), 128.54 (a), 130.50 (b), 162.32 (d).

[0057] $^{19}\text{F-NMR}$ (471 MHz) : at -221.65 (s, 3F), -121.18 (s, 6F), -225.55 (s, 2F, g or j) - 209.76 (s, 2F, j or g), -121.07 (s, 2F, k), -116.72 (q, 6F, i), -114.03 (d, 2F, h)

[0058] In addition, the results of gas-chromatography mass spectrometric analysis were 486 (M^+ , 1.4%), 400 (1.4%), 381 (2.4%), 181 (7.1%), 86 (100%).

[0059] The melting point measured by DSC (differential scanning calorimetry) was 54.7 to 57.1°C.

[0060] As the result of structural analysis by the above-mentioned spectroscopic data, the following structural formula has been confirmed.



Example 5

[0061] In a 500 mL Kjeldahl flask was placed 62.3 g (150 millimol) of 1,3-perfluoroadamantandiol¹⁾, to which was added 200 mL of diethyl ether to dissolve the same. Thereafter the flask was put in an ice bath, and 25.1 mL (180 millimol) of triethylamine and 12.2 mL (150 millimol) of methacrylic acid chloride were added in the flask to start stirring. After the lapse of 1 hour, the ice bath was taken out, and the contents therein were reacted for further 15 hours at room temperature. The reaction liquid was filtered with fluted filter paper, and the flask was washed twice with 50 mL of diethyl ether. Salts were removed from the reaction liquid with a separatory funnel to recover organic phase. Then by evaporating away the solvent and purifying with a column, the objective 3-hydroxy-1-perfluoroadamantyl acrylate²⁾ [actual yield amount of 18.6 g (39.2 millimol), yield rate of 26.1% and purity measured by gas chromatography being 96.5% {area}] and 1,3-perfluoroadamantyl diacrylate [actual yield amount of 8.6 g (16.2 millimol), yield rate of 10.8% and purity measured by gas chromatography being 95.3% {area}] were obtained,

1): contains 2-hydro-1,3-perfluoroadamantandiol by 25.4% as an impurity.

2): 3-hydroxy-1-perfluoroadamantyl acrylate and 1,3-perfluoroadamantyl diacrylate contain as impurities, 2-hydro-3-hydroxy-1-perfluoroadamantyl acrylate by 10.7% and 2-hydro-1,3-perfluoroadamantyl diacrylate by 18.7%, respectively.

[0062] As a result of analysis for the resultant 3-hydroxy-1-perfluoroadamantyl acrylate by nuclear magnetic resonance spectra (NMR, CDCl_3), there were observed the following absorption.

[0063] $^1\text{H-NMR}$ {500 MHz} : at 4.95 (br, 1H), 6.14 (d, $J=10.1$ Hz, 1H),

6.24 (dd, $J=10.1$ Hz, 1H, $J=17.2$ Hz, 1H), 6.62 ($J=17.2$ Hz, 1H),

[0064] $^{13}\text{C-NMR}$ {126 MHz} : at 125.88 ($\text{CH}_2=$), 135.96 ($-\text{CH}=$), 158.05 ($\text{C}=\text{O}$),

[0065] $^{19}\text{F-NMR}$ {471 MHz} : at -219.30 (s, 2F), -120.69 (s, 6F), -113.61 (s, 6F)

[0066] In addition, as the results of infrared spectroscopy (IR), absorption was observed at 1765.6 cm^{-1} ($\text{C}=\text{H}$).

[0067] The melting point measured by DSC (differential scanning calorimetry) was 69.7 to 79.5°C .

[0068] As a result of analysis for the resultant 1,3-perfluoroadamantyl diacrylate by nuclear magnetic resonance spectra (NMR, CDCl_3), there were observed the following absorption.

[0069] $^1\text{H-NMR}$ {500 MHz} : at 6.12 (d, $J=10.9$ Hz, 2H), 6.24 (d, d, $J=10.9$ Hz, $J=16.6$ Hz, 2H), 6.62 ($J=16.6$ Hz, 2H)

[0070] $^{13}\text{C-NMR}$ {126 MHz} : at 126.09 ($\text{CH}_2=$), 135.78 ($-\text{CH}=$), 161.55 ($\text{C}=\text{O}$),

$^{19}\text{F-NMR}$ {471 MHz} : at -219.01 (t, $J=29$ Hz, 2F), -121.19 (s, 2F), -120.49 (d, $J=249$ Hz, 2F), -119.07 (d, $J=264$ Hz, 2F), -117.19 (d, $J=249$ Hz, 2F), -113.81 (d, $J=29$ Hz, 2F), -113.49 (d, $J=264$ Hz, 2F)

[0071] In addition, as the results of infrared spectroscopy (IR), absorption was observed at 1781.8 cm^{-1} ($\text{C}=\text{H}$).

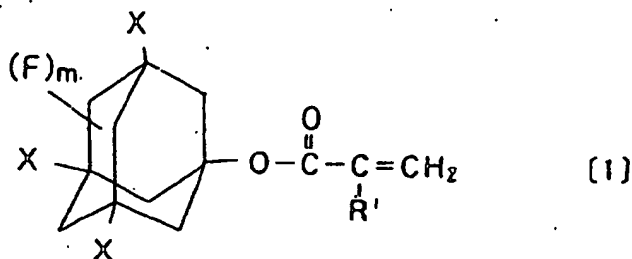
[0072] The melting point measured by DSC (differential scanning calorimetry) was 92.4 to 106.7°C .

INDUSTRIAL APPLICABILITY

[0073] The present invention can provide a perfluoroadamantyl acrylate compound which is highly useful in wide fields of raw materials for functional resins required of optical properties and heat resistance; resin additives such as heat resistance improvers; additives such as acidity enhancers and fat-solubility enhancers; coating materials such as paint and printing ink; lubricating oil; working oil; heating / heat transfer media; adhesives; covering materials for optical fiber; pharmaceuticals; agrochemicals; intermediates and so forth.

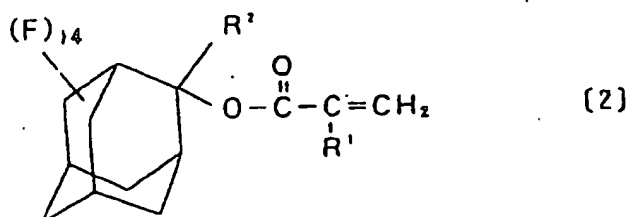
Claims

1. A perfluoroadamantyl acrylate compound represented by the following general formula (1)



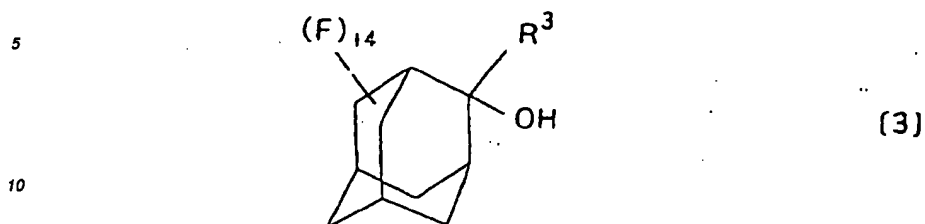
wherein R^1 is a hydrogen atom, a methyl group or a trifluoromethyl group; X is a fluorine atom, a hydroxy group or a $\text{CH}_2=\text{C}(\text{R})\text{COO}$ group, wherein R is a hydrogen atom, a methyl group or a trifluoromethyl group; and m is an integer of from 12 to 15.

2. A perfluoroadamantyl acrylate compound represented by the following general formula (2)



wherein R^1 is a hydrogen atom, a methyl group or a trifluoromethyl group; and R^2 is a hydrogen atom, a methyl group, an ethyl group or a perfluoroalkyl group having 1 to 4 carbon atoms.

3. A perfluoroadamantanol compound represented by the following general formula (3)



15 wherein R³ is a methyl group, an ethyl group or a perfluoroalkyl group having 1 to 4 carbon atoms.

20

25

30

35

40

45

50

55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/13378

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ C07C69/653, 35/52		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ C07C69/653, 35/52		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAPLUS (STN), REGISTRY (STN)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Adcock, James L. et al., Highly Fluorinated Adamantanols: Synthesis, Acidities, and Reactivities, Journal of Organic Chemistry, 1996, Vol.61, No.15, pages 5073 to 5076	1-3
A	Adcock, James L. et al., Synthesis and nucleophilic and photochemical reactions of F-adamantanone, Journal of Organic Chemistry, 1992, Vol.57, No.15, pages 4297 to 4300	1-3
A	JP 63-307844 A (Hakusui Kagaku Kogyo Kabushiki Kaisha), 15 December, 1988 (15.12.88), (Family: none)	1-3
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 20 February, 2003 (20.02.03)		Date of mailing of the international search report 11 March, 2003 (11.03.03)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)